Arabian Journal of Chemistry (2015) **xxx**, xxx–xxx

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Electrochemical detection of lead (II) at bismuth/Poly(1,8-diaminonaphthalene) modified carbon paste electrode

Fatima Ezzahra Salih, Aicha Ouarzane, Mama El Rhazi *

Laboratory of Physical Chemistry & Bioorganic Chemistry, Faculty of Sciences and Technologies – BP 146, Mohammedia 20650, University Hassan II Casablanca, Morocco

Received 29 May 2015; accepted 15 August 2015

KEYWORDS

Electrochemical sensor;
Carbon paste electrode;
Poly(1,8-Diaminonaphthalene);
Bismuth film;
Lead

Abstract A new sensor based on carbon paste electrode modified with Poly(1,8-diaminonaphthalene) and bismuth film (Bi-Poly1,8-DAN/CPE) was prepared and characterized with cyclic voltammetry and electrochemical impedance spectroscopy. The sensor was found to exhibit an electroactivity toward the sensing of lead using square wave voltammetry in acidic medium. Various operational parameters, such as concentration of Bi(III), square wave voltammetric parameters, deposition potential and deposition time were investigated. Under the optimized conditions, a linear range was achieved over concentration range from 0.5 μg L^{-1} to 50 μg L^{-1}, with a detection limit of 0.3 μg L^{-1} offering a good repeatability and reproducibility. Finally, the Bi-Poly1,8-DAN/CPE was applied for the analysis of lead in water samples with satisfactory results.

1. Introduction

Excessive levels or even small doses of very toxic metals (i.e. lead, cadmium, mercury) can cause several damages on the environment and human health. Therefore sensitive and selective methods for the detection of heavy metals especially lead have become a priority in environmental monitoring. During the last decades, different approaches have been used to develop high-performance electrochemical sensors based on bismuth film or conducting polymers (Hwang et al., 2008a,b; Kefala and Economou, 2006; Yi et al., 2012). Since the pioneering work of Wang (Wang et al., 2000), Bismuth film electrode called environmentally friendly electrode has been widely used in organic, biological and pharmaceutical analysis (Chatzitheodorou et al., 2004; de Lima and Spinelli, 2013; Jain and Sharma, 2012; Pierini et al., 2013). Detections of heavy metals especially lead using voltammetric techniques and bismuth film electrodes have been reported in some excellent reviews (Arduini et al., 2010; Baldrianova et al., 2007; Lezi et al., 2012; Švancara et al., 2010; Wang, 2005). Consequently, Bismuth has been introduced as an alternative working electrode material, and it has a property to form binary or

* Corresponding author. Tel.: +212 61404127; fax: +212 23315353.
E-mail address: elrhazim@hotmail.com (M. El Rhazi).

Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2015.08.021

multi-component alloy with some heavy metals commonly known as fused alloy, facilitating the nucleation process during deposition of heavy metal ions.

The modification of the electrode by organic conducting polymers has also been a very active area of research. Organic conducting polymers received great attention due to their potential application as electrochemical sensors (Ates and Sarac, 2009; Bai et al., 2009; Shahrokhian et al., 2015). Philips et al., demonstrated that the chelating cyano group containing polyaniline derivative could be an effective electrode for ultra-sensitive electrode for detection of lead and cadmium (Philips et al., 2012). The electrochemical modification of glassy carbon with electropolymerized form of 1,10-phenanthronine for voltammetric determination of cadmium was reported by Oztekin et al. (2011). The sensitivity of Poly(1,8- diaminonaphthalene) to heavy metal ions such as Ag^{+}, Hg^{2+} and Cu^{2+} has been studied using electrochemical and spectroscopic methods. The ability of conducting polymer matrices to complex heavy metals was studied by different groups. It has been proved that metal ions form complexes with amino groups of the polymer (El Rhazi and Majid, 2014; Nguyen et al., 2011).

More recently, the combination of metallic ions with polymers has been investigated to improve the properties of these materials for electroanalytical purposes. Ojani et al., reported that the combination of 1,5-diaminonaphthalene and Nickel particles improves the oxidation of methanol (Ojani et al., 2008). In another study, Hathoot et al., prepared and characterized the Poly1,5-diaminonaphthalene on the surface of carbon electrode using cyclic voltammetry. After electropolymerization, the transition metal ions of Ni (II) were incorporated to the polymer for the electrocatalytic oxidation and simultaneous determination of glucose, ascorbic acid and dopamine (Hathoot et al., 2012). A Bi/Nafion/overoxidized 2-mercaptoethanesulfo nate-tethered polypyrrole/glassy carbon electrode has been developed to simultaneous determination of cadmium and lead (Chen et al., 2014). The composite film is of great interest because of their strong electronic interactions between the metallic particles and the polymer matrices (Henríquez et al., 2012; Kokkinos and Economou, 2011; Li et al., 2009; Piankova et al., 2011; Yang et al., 2014). It has been reported that the electrocatalytic properties of nanoparticles could be improved by the conductive polymeric matrices (Balazs et al., 2006; Švancara et al., 2006; Wang et al., 2013; Yang et al., 2013).

Motivated by the striking properties of Poly1,8-diaminonaphthalene into carbon paste electrode and the wide uses of bismuth film electrode in electroanalysis, we decided to combine the advantageous feature of our conducting polymer and bismuth film for a detection of lead. At our best knowledge, the combination of 1,8-diaminonaphthalene (1,8-DAN) and bismuth was not studied. Herein, for the first time facile approaches for synthesis of Bi-Poly1,8-DAN were proposed. At the first step, the electropolymerization of 1,8-DAN into carbon paste electrode was conducted in acidic media free of monomer. The electrode surface could be renewed by simple extrusion of a small amount of paste from the tip of the electrode and the polymer could be renewed very easily. Then, the bismuth film electrode was deposited at negative potential. For determination of lead, the Poly (1,8-DAN) was modified with *in situ* plated bismuth film electrode and the performance of prepared sensor was then evaluated in real water samples using square wave anodic stripping voltammetry.

2. Experimental section

2.1. Reagents and materials

The chemical reagents used in the preparation of stock solutions were of analytical reagent grade. 1,8-Diaminonaphthalene (1,8-DAN) was obtained from Sigma Aldrich. All solutions were diluted by distilled water. Supporting electrolyte was solution of hydrochloric acid. Bismuth Stock solution of 100 mg L^{-1} was prepared from $Bi(NO_3)_2$ṡ$5H_2O$ (Sigma Aldrich), whereas $Pb(NO_3)_2$ (Riedel–Dehaen) was employed in the preparation of metal-ion stock solution with concentration of 100 mg L^{-1}.

2.2. Instrumentation

Voltammetric measurements (cyclic voltammetry (CV), square wave voltammetry (SWV)) and Electrochemical Impedance Spectroscopy (EIS) were performed using AUTOLAB PGSTAT302 N (EcoChemie, Utrecht, Netherlands) Potentiostat/Galvanostat controlled by GPES 4.9 software. The three-electrode system configuration includes a carbon paste as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum disk as the counter electrode. The pH was adjusted by addition of NaOH or HCl solution using a Fisher Scientific Accumet AB15 Basic pH meter.

2.3. Preparation of working electrode

A 1,8-Diaminonaphthalene doped carbon paste electrode (1,8-DAN/CPE) was fabricated as follows: 1% (w/w) of 1,8-DAN dissolved in a small quantity of acetonitrile, thoroughly homogenizing with 1 g graphite powder and 30% (w/w) paraffin oil using a mortar and pestle. The paste mixture was packed into electrode cavity 2 mm (Teflon-PTFE tube, ϕ = 3 mm) and electrical contact was established with a copper rod. The surface of the 1,8-DAN/CPE was polished on a piece of white paper. The bare carbon paste electrode (CPE) was fabricated with the same way without addition of the monomer. The Bi-Poly1,8-DAN/CPE and BiF-CPE were prepared by *in situ* plating bismuth in the detection step.

2.4. Procedures

Electropolymerization was performed at a constant potential of 0.7 V (vs. SCE) for 80 s in 0.1 M HCl solution. Following the polymerization, the electrode was cycled in 0.1 M HCl solution free of monomer for five scans until a stable voltammogram was obtained. The conditions employed will be reported in the discussion.

In square wave anodic stripping voltammetric (SWASV) measurements, the modified electrode by Poly1,8-DAN was dipped into 0.1 M HCl solution containing 500 μg L^{-1} Bi (III) and predetermined concentration of target Pb(II). A deposition potential of −1 V (vs. SCE) and a deposition time of 120 s were applied to the working electrode under stirring conditions. The stirring was stopped and after 10 s equilibration time, the square wave anodic stripping voltammograms (SWASV) were recorded between −0.7 and −0.3 V (with a step increment of 5 mV and amplitude of 50 mV). For repetitive

Please cite this article in press as: Salih, F.E. et al., Electrochemical detection of lead (II) at bismuth/Poly(1,8-diaminonaphthalene) modified carbon paste electrode. Arabian Journal of Chemistry (2015), http://dx.doi.org/10.1016/j.arabjc.2015.08.021

measurements, the electrode surfaces were cleaned after each measurement at 0.3 V (vs. SCE) for 30 s with continuous stirring to remove the residual metals on the electrodes prior to the next measurement.

3. Results and discussion

3.1. Electropolymerization of the polydiaminonaphthalene on carbon paste electrode

The synthesis and characterization of Poly1,8-DAN were investigated using potentiostatic mode and cyclic voltammetry. The oxidation potential of DAN is an important parameter for the electropolymerization, and it can be determined easily on the basis of the first scan of cyclic voltammogram during the electropolymerization. Since it is well known, that a well-defined anodic peak could be observed at 0.6 V (vs. SCE) for the first scan during electropolymerization of diaminonaphthalene as described elsewhere (Majid et al., 2003), the electropolymerization of Poly1,8-DAN was carried out in 0.1 M HCl solution at a constant potential of +0.7 V (vs. SCE) for 80 s. Following the polymerization, the electrode was cycled in 0.1 M HCl solution for five scans between −0.5 and 0.9 V at a sweep rate of 50 mV s^{-1}. Both cathodic and anodic currents increase, indicating continuous polymerization as shown in Fig. 1. The cyclic voltammograms of obtained polymer recorded during the five scans on carbon paste electrode are in accordance with our previous results (Majid et al., 2003) using cyclic voltammetry during 40 cycles (which is time consuming) indicating that the obtained polymer is conducting. The structure of formed polymer was reported with details in the literature (El Rhazi and Majid, 2014; Lee et al., 1992; Oyama et al., 1989) using anodic oxidation in both acidic and acetonitrile solutions.

3.2. Electrochemical behavior of the Poly1,8-DAN modified carbon paste electrode

Cyclic voltammetry was employed to investigate the electrochemical behavior on the CPE and Poly1,8-DAN/CPE in a 1.0 mM in $[Fe(CN)_6]^{3-/4-}$ solution. Fig. 2 illustrates the responses obtained by cyclic voltammetry between −0.1 and +0.7 V at CPE (a), and Poly1,8-DAN/CPE (b). At CPE, a weak redox peak response was observed with ΔEp equal to 302 mV (vs. SCE). While at Poly1,8-DAN/CPE, the redox peak separation was found to be small 137 mV (vs. SCE) indicating a better electrochemical reversible behavior on Poly1,8-DAN/CPE. The redox currents responses of $[Fe(CN)_6]^{3-/4-}$ at Poly1,8-DAN/CPE were also higher (Ip_a = 243.04 μA et Ip_c = −265.28 μA) than CPE which implied that the electron transfer rate at Poly1,8-DAN/CPE was significantly improved.

3.3. Electrochemical impedance spectroscopy

It is well known that the Electrochemical impedance spectroscopy (EIS) technique is a powerful technique to characterize the electrochemical process that occurs at the electrode/solution interface. Therefore, the electrochemical properties of bare and modified electrode were evaluated by studying redox behavior of $[Fe(CN)_6]^{3-/4-}$ couple using EIS techniques. The impedance measurements were performed in the presence of 1.0 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl solution at scanning frequency from 0.05 to 10,000 Hz. Fig. 3 shows the EIS diagrams of the CPE and Poly1,8-DAN/CPE. The Nyquist plot of impedance spectra includes a semicircle portion at higher frequencies corresponding to the electron transfer limited process. The charge transfer resistance (R_{CT}) is known as a useful parameter reflecting the facility of electrode reaction, which can be measured by EIS from the semicircle diameter in the Nyquist plots (Yang and Li, 2005). The EIS tests have confirmed the conclusions deduced from the above CV experiments. The obtained values of charge transfer resistance (R_{CT}) were 106.2 KΩ, 3.67 KΩ and the constant phase element was 16.60 μF cm^{-2} and 209.54 μF cm^{-2} for CPE and Poly1,8-DAN/CPE, respectively, suggesting that the surface of the Poly1,8-DAN/CPE exhibits lower electron-transfer resistance and increases the electron transfer rate

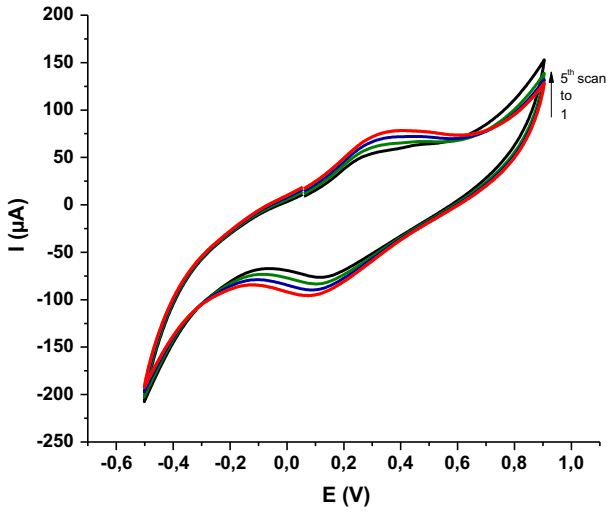

Figure 1 Cyclic voltammograms following the potentiostatic polymerization mode of Poly1,8-DAN/CPE recorded at room temperature in 0.1 M HCl solution at scan rate of 50 mV s^{-1}.

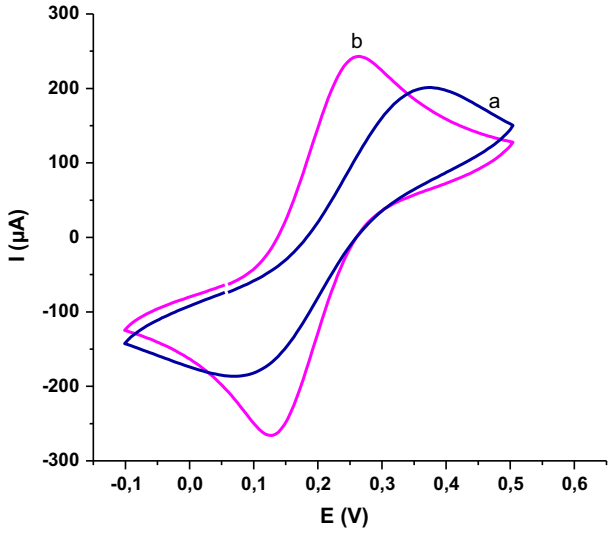

Figure 2 Comparison of the cyclic voltammetric behavior at modified electrode in 1.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ + 0.1 M KCl solution, (a) CPE, (b) Poly1,8-DAN/CPE.

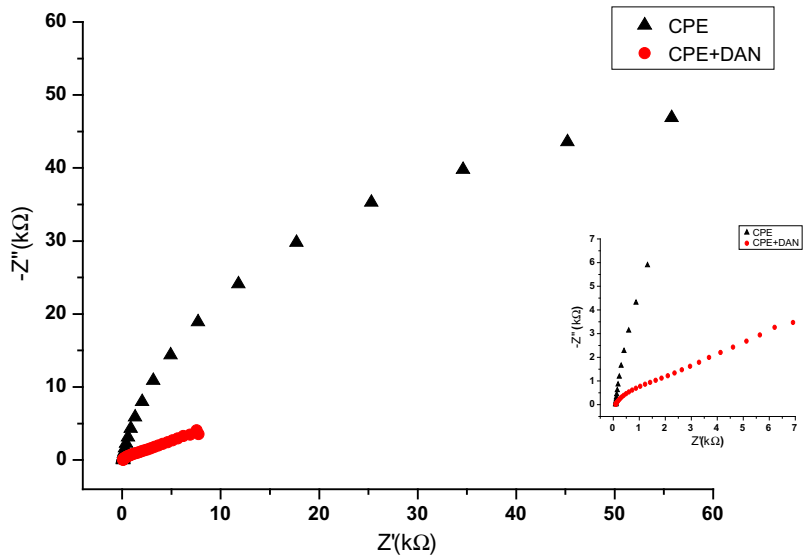

Figure 3 A Nyquist plots of CPE ((a) triangle), Poly1,8-DAN/CPE ((b) circle) in 1.0 mM $Fe(CN)_6^{3-/4-}$ in 0.1 M KCl solution.

(Dong et al., 2012). The same results were obtained by Jain et al. (2014) at PANI–Bi_2O_3/GCE characterized by high electrocatalytic activity due to the lower charge transfer resistance.

3.4. Square-wave anodic stripping voltammetric analysis of Pb (II)

After the characterization of the electrodes, the ability of such electrode to detect lead was investigated. Preliminary experiments were carried out on different electrodes. CPE, Poly1,8-DAN/CPE were dipped in solution containing 100 μg L^{-1} of Pb(II) with or without 1000 μg L^{-1} bismuth concentration. The comparison between the square wave anodic stripping voltammetric responses on a BiF-CPE (solid line), Bi-Poly1,8-DAN/CPE (dotted line) and Poly1,8-DAN/CPE (dash line) is shown in Fig. 4, indicated that the sensitivity was higher on the Bi-Poly1,8-DAN/CPE. The results demonstrated that the peak height of Pb(II) has 20% of improvement on the Bi-Poly1,8-DAN/CPE over the BiF-CPE. Similar results have been observed by Cao et al. (2008) at bismuth-modified zeolite doped carbon paste electrode against BiF-CPE and Luo et al., at bismuth-modified multiwalled carbon nanotubes doped carbon paste electrode (Luo et al., 2013). A considerable difference was observed between Poly1,8-DAN/CPE with and without bismuth film. Furthermore, the Bi-Poly1,8-DAN/CPE showed good reproducibility of stripping current of Pb(II).

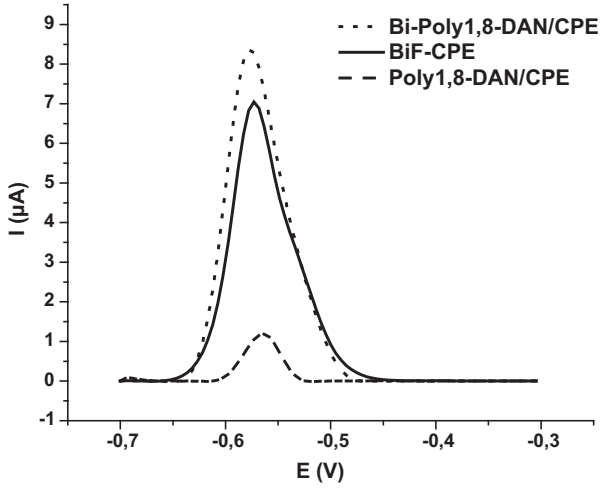

Figure 4 SWASVs for Poly1,8-DAN/CPE (dash line), BiF-CPE (solid line) and Bi-Poly1,8-DAN/CPE (dot line) in solution with 100 μg L^{-1} of Pb(II) in the absence and presence of 1000 μg L^{-1} Bi (III). The stripping step is applied via a potential sweep from −0.7 to −0.3 V. Supporting electrolyte 0.1 M HCl, deposition potential −1 V, deposition time 120 s.

The interaction mechanism of formed Poly1,8-DAN with lead ions can be explained by the complex formation between lead, bismuth and diaminonaphthalene (Mariame et al., 2009). Moreover, the enhanced stripping response at the modified electrode was also attributed to the fact that during the deposition step, the bismuth form "fused alloys" with lead making him more readily to be reduced. The combination of bismuth film with polymer improves the SWASV response of lead as reported by different authors (Kefala et al., 2004; Xu et al., 2008; Yang et al., 2014).

3.5. Effect of experimental variables

3.5.1. Effect of the concentrations of Bi(III)

Stripping performance of the Bi-Poly1,8-DAN/CPE was also studied with respect to the dependence of the electrode response for 50 μg L^{-1} of Pb(II) on the concentration of bismuth ions in the measurement solution. The effect of the concentration of the Bi(III) was examined in the range from 50 to 1000 μg L^{-1}, with potential and deposition time of −1 V (vs. SCE) and 120 s, respectively. From Fig. 5, it is evident that even at low concentration ([Bi (III)] ≈ 50 μg L^{-1}), the response of the Bi-Poly1,8-DAN/CPE toward Pb(II) was very sensitive. As the concentration of Bi(III) increased, the peak currents of Pb(II) attained a maximum value at about 250–500 μg L^{-1} Bi(III) and then decreased at higher concentrations. The Bi(III)/metal ion concentration ratio in the 1–10 range was adequate on bismuth film-plated CPEs as reported by Baldrianova et al.

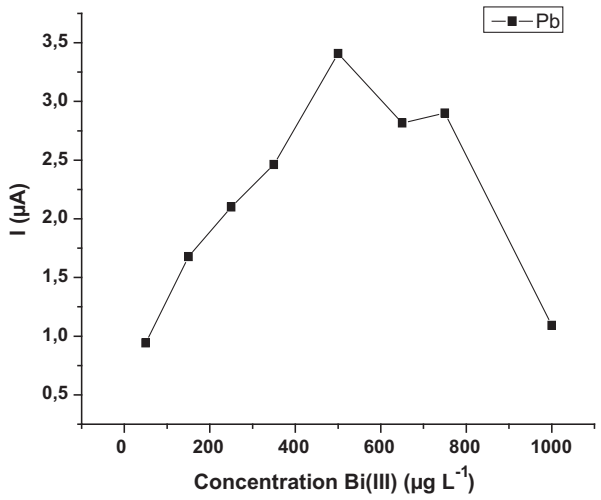

Figure 5 The effect of the Bi(III) concentrations on the stripping currents of Pb(II) at a Bi-Poly1,8-DAN/CPE. The Bi(III) concentration varies from 50 to 1000 µg L^{-1} range. Other conditions as in Fig. 4.

(2006). In general the Bi concentration 10-fold the concentration of metal was the optimum for the thickness of bismuth film, and this result is consistent with previous report on bismuth film-plated CPEs (Švancara et al., 2006). Therefore, the Bi(III) concentration of 500 µg L^{-1} was selected for the rest of this work.

3.5.2. Optimization of SWV conditions

The influence of square-wave voltammetry parameters was also explored to find the optimal values of amplitude, frequency and step increment that implies a good Pb signals. First, the amplitude was varied in the range of 10–100 mV, fixing the frequency at 25 Hz. The peak current of lead increased with increasing amplitude up to 50 mV. At amplitude more than 60 mV, deformation of the peaks of bismuth and lead was observed with significant increase in peaks width. Therefore, 50 mV was chosen as the square-wave amplitude. The potential step increment together with the frequency defines the effective scan rate. The frequency was varied in the range of 10–100 Hz and the responses for lead increased with frequency in this range. No deformation in the voltammetric shape of lead oxidation and any significant reduction in peak current were observed. By fixing amplitude of 50 mV and a frequency of 50 Hz, the effect of potential step increment was studied, in the range of 1–10 mV. For potential steps lesser than 7 mV, the current peak increased in height and the peak current decreased slowly for potential steps greater than 8 mV. Hence, a frequency of 50 Hz and 5 mV potential step increment were chosen. Therefore, high and reproducible signals of Pb(II) were obtained with these parameters, the result seems to be similar compared to those found by Dimovasilis and Prodromidis. (Dimovasilis and Prodromidis, 2013) using a bismuth-modified (3-mercaptopropyl) trimethoxysilane (MPTMS).

3.5.3. Effect of the deposition potential and the preconcentration time

The influence of the deposition potentials on metal stripping signal was studied with 50 µg L^{-1} of Pb(II) with deposition time of 120 s in the range from −0.8 up to −1.4 V. The results showed that the stripping currents of Pb(II) moderately increased when the accumulation potential shifted from −0.8 to −1.1 V. When the deposition potential applied become more negative than −1.1 V (vs. SCE) (Fig. 6), the peak currents of Pb(II) and Bi become poor and we observe the appearance of bubbles on the electrode surface because hydrogen evolution is beginning to be significant at such negative potential as reported elsewhere (Kokkinos and Economou, 2011). The hydrogen bubbles might damage the metal alloys deposited on the electrode surface and lead to decrease in current signals at very negative potentials. Consequently, −1 V (vs. SCE) was selected for the following experiments.

The preconcentration time was studied in the range 30–300 s for solution containing 50 µg L^{-1} of Pb(II) in HCl 0,1 M solution. The stripping currents of Pb(II) increased up to 210 s, after this deposition time the peak current decreased slowly as shown in Fig. 7.

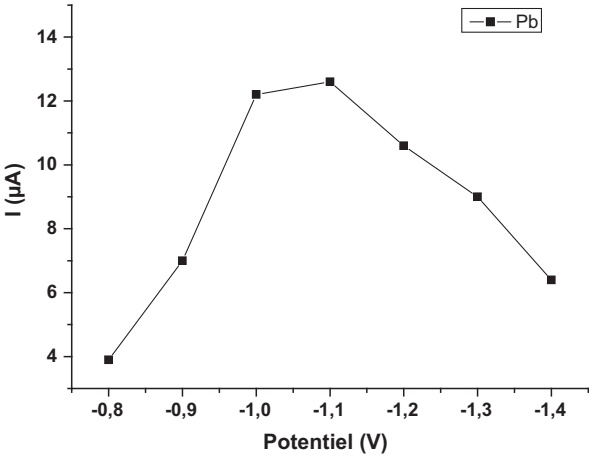

Figure 6 The effect of deposition potential on the stripping currents of 50 µg L^{-1} Pb(II) at the Bi-Poly1,8 DAN/CPE in 0.1 mol L^{-1} 0,1 M HCl solution containing 500 µg L^{-1} Bi(III).

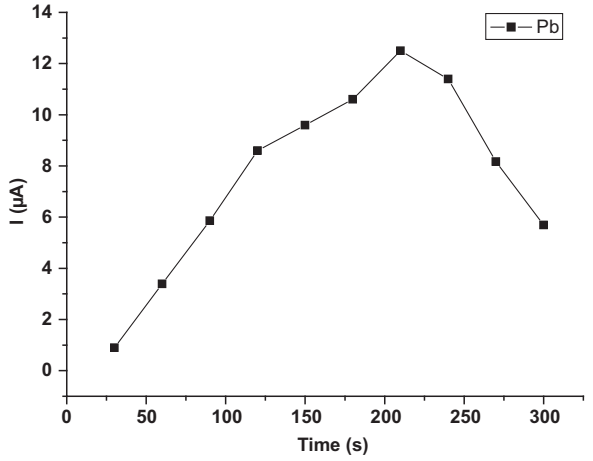

Figure 7 The effect of deposition time on the stripping currents of 50 µg L^{-1} Pb(II) at the Bi-Poly1,8 DAN/CPE in 0.1 mol L^{-1} 0,1 M HCl solution containing 500 µg L^{-1} Bi(III).

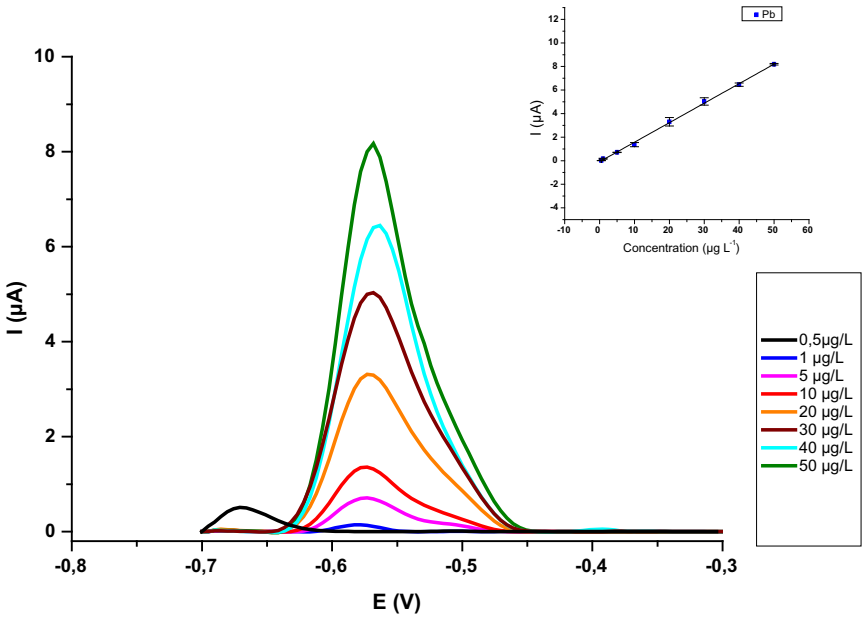

Figure 8 SWASVs for different concentrations of Pb(II) on *in situ* deposited Bi-poly1,8-DAN/CPE in the presence of 500 μg L^{-1} Bi(III). From bottom to top 0.5, 1, 5, 10, 20, 30, 40 and 50 μg L^{-1} Pb(II), Supporting electrolyte 0.1 M HCl solution, deposition potential −1 V, deposition time 120 s, amplitude 50 mV, increment potential 5 mV, quiet time 10 s. (Inset) the calibration curve of Pb(II). Results are presented with error bar of triplicate experiments.

3.6. Calibration

Under the optimized experiment conditions, the calibration curve for the determination of Pb(II) in HCl 0,1 M solution on the Bi-Poly1,8-DAN/CPE was achieved by SWASV analysis with a preconcentration time of 120 s. The resulting stripping voltammograms for different concentrations of lead are illustrated in Fig. 8. The linear regression equation was $Ip = 0.165\ C_{Pb} - 0.086$ with a high correlation coefficient of 0.9986 in the concentration range comprised between 0.5 μg L^{-1} and 50 μg L^{-1} for Pb(II). The standard deviation of the mean value for 10 voltammograms of the blank and, the slope from the calibration curve were used to determine the limit of detection (LOD) according to IUPAC recommendations (Committee and others, 1987; Miller and Miller, 2005). Then, the determinate limit of detection (LOD) for Pb(II) was 0.3 μg L^{-1}. The obtained value exhibited a comparable and sometimes better LOD compared to some Bi modified electrodes published in the literature (see Table 1). The repeatability of the modified electrode was performed with the same electrode in a solution containing 50 μg L^{-1} Pb(II) with 500 μg L^{-1} Bi(III). The relative standard deviation (R.S.D.) of five replicates samples was 4.32%. The reproducibility of the method was also evaluated by preparing five modified electrodes at different days using the same procedure. The RSD value calculated performing the determination of 50 μg L^{-1} Pb(II) by SWASV was 4,6%.

Table 1 Analytical parameters and limits of detection at some Bi-film modified sensors in the determination of lead ions.

Substrate electrode	Technique	Potential deposition (V)	Temps deposition (s)	Detection limit (μg L^{-1})	References
Bi/Nafion/OPPy–MES/GCE	SWV	−1.2	300	0.03	(Chen et al., 2014)
GCE-MWCNT/poly(PCV)/Bi	DPASV	−1.3	420	0.40	(Chamjangali et al., 2015
SbF-CPE	ASV	−1.2	120	0.2	Tesarova et al., 2009
MMT/BiCE	SWASV	−1.2	120	0.2	(Luo et al., 2010)
Pt/MWCNT/P1,5-DAN electrode	SWASV	−1.2	420	2.1	(Vu et al., 2015)
BiOCl/MWNT-GCE	SWASV	−1.2	120	0.57	(Cerovac et al., 2015)
GCE/Bi-xerogel/Nafion	SWASV	−1.2	240	1.3	(Dimovasilis and Prodromidis, 2013)
Bi/Au–GN–Cys/GCE	SWASV	−1.2	800	0.05	(Zhu et al., 2014)
Bi/CPE	SWASV	−1	300	0.9	(Hočevar et al., 2005)
Porous antimony film electrode	ASV	−1.2	100	0.5	(Urbanová et al., 2010)

MES: mercaptoethanesulfonate, PPy: polypyrrole, GCE: glassy carbon electrode, PCV: Pyrocatechol violet, MWCNT: multi-walled carbon nanotube, Sb: Antimony, CPE: carbon paste electrode, MMT: montmorillonite, 1,5-DAN:1,5-Diaminonaphthalene, BiOCl: bismuth-oxy-chloride, Au–GN–Cys: gold nanoparticle–graphene–cysteine, Bi: bismuth.
SWASV: square wave anodic stripping voltammetry, SWV: square wave voltammetry, DPASV: differential pulse anodic stripping voltammetry.

Please cite this article in press as: Salih, F.E. et al., Electrochemical detection of lead (II) at bismuth/Poly(1,8-diaminonaphthalene) modified carbon paste electrode. Arabian Journal of Chemistry (2015), http://dx.doi.org/10.1016/j.arabjc.2015.08.021

Table 2 Determination of Pb(II) in real samples: tap water and water well.

	Original $\mu g\ L^{-1}$	Added $\mu g\ L^{-1}$	Found $\mu g\ L^{-1}$	Recovery %	R.S.D. (%)
Water Well	ND	5	5.01	100.2	1.8
	ND	10	10.9	109.2	4.3
Tap water	ND	5	5.34	106.9	4.4
	ND	10	10.1	100.7	3.9

ND: Not detected.

3.7. Interference study

The interferences from other metal ions were investigated, which can compete and codeposited with Pb(II) at the active sites on the electrode surface. The Cu(II) a major interfering substance has a significant effect on the stripping currents of the bismuth electrodes. Due to the competition between bismuth and copper, the presence of Cu(II) affected greatly the Pb(II) peak which was evident even at a twofold concentration of Cu(II) over Pb(II). This is probably related to the fact that bismuth and copper have nearly reduction potential and that copper forms stable complex with poly(1,8 DAN). This interference was alleviated by the addition of 0.1 mM of potassium ferrocyanide ions that form a stable complex with Cu(II), then lead peak recovered its original level and even higher (Hwang et al., 2008b). Other metals such as Cd(II), Zn(II), Fe(II), even at a ten-fold excess over Pb(II) did not affect the stripping peak of Pb(II).

3.8. Application

In order to evaluate the performance of Bi-Poly1,8-DAN/CPE, the determination of Pb (II) was carried out in two real samples from our local environment, well and tap water. The water samples were collected and adjusted to pH < 2 without any other pretreatment. No lead traces were found using the proposed procedure and under the optimized conditions. Then, the standard addition method was used and known amounts of lead were spiked to the water samples in triplicate ($n = 3$) according the SWASV procedure described in experimental section. Table 2 summarizes the recoveries of the results obtained for two replicate determinations of 5 $\mu g\ L^{-1}$ and 10 $\mu g\ L^{-1}$ in tap water and well water. The results given in Table 2 indicate good recoveries between 100% and 109%. The good values observed in the recovery procedure show that the proposed method is suitable for the determination of Pb(II) in real water samples.

4. Conclusion

In this work, we have shown the advantageous features of poly (1,8-DAN) modified carbon paste electrode combined to the bismuth film. A novel electrode has been proposed which is rapid, simple, easy to prepare compared with other reported methods. The possibility of the Bi-Poly1,8-DAN/CP electrode for the determination of Pb(II) has been investigated using SWASV. The Bi-Poly1,8-DAN/CP electrode exhibited better results compared to commonly used BiF-CP and Poly1,8-DAN/CP electrodes due to the conducting polymer formed at the surface of the electrode and bismuth film advantage. The sensor has been successfully applied to the determination of lead ions in real water samples.

References

Arduini, F., Calvo, J.Q., Palleschi, G., Moscone, D., Amine, A., 2010. Bismuth-modified electrodes for lead detection. TrAC Trends. Anal. Chem. 29, 1295–1304.

Ates, M., Sarac, A.S., 2009. Conducting polymer coated carbon surfaces and biosensor applications. Progr. Organ. Coat. 66, 337–358.

Bai, H., Zhao, L., Lu, C., Li, C., Shi, G., 2009. Composite nanofibers of conducting polymers and hydrophobic insulating polymers: preparation and sensing applications. Polymer 50, 3292–3301.

Balazs, A.C., Emrick, T., Russell, T.P., 2006. Nanoparticle polymer composites: where two small worlds meet. Science 314, 1107–1110.

Baldrianova, L., Svancara, I., Vlcek, M., Economou, A., Sotiropoulos, S., 2006. Effect of Bi(III) concentration on the stripping voltammetric response of *in situ* bismuth-coated carbon paste and gold electrodes. Electrochim. Acta 52, 481–490.

Baldrianova, L., Svancara, I., Sotiropoulos, S., 2007. Anodic stripping voltammetry at a new type of disposable bismuth-plated carbon paste mini-electrodes. Anal. Chim. Acta 599, 249–255.

Cao, L., Jia, J., Wang, Z., 2008. Sensitive determination of Cd and Pb by differential pulse stripping voltammetry with *in situ* bismuth-modified zeolite doped carbon paste electrodes. Electrochim. Acta 53, 2177–2182.

Cerovac, S., Guzsvány, V., Kónya, Z., Ashrafi, A.M., Švancara, I., Rončević, S., Kukovecz, Á., Dalmacija, B., Vytřas, K., 2015. Trace level voltammetric determination of lead and cadmium in sediment pore water by a bismuth-oxychloride particle-multiwalled carbon nanotube composite modified glassy carbon electrode. Talanta 134, 640–649.

Chamjangali, M.A., Kouhestani, H., Masdarolomoor, F., Daneshinejad, H., 2015. A voltammetric sensor based on the glassy carbon electrode modified with multi-walled carbon nanotube/poly(pyrocatechol violet)/bismuth film for determination of cadmium and lead as environmental pollutants. Sens. Actuat. B: Chem. 216, 384–393.

Chatzitheodorou, E., Economou, A., Voulgaropoulos, A., 2004. Trace determination of chromium by square-wave adsorptive stripping voltammetry on bismuth film electrodes. Electroanalysis 16, 1745–1754.

Chen, L., Li, Z., Meng, Y., Zhang, P., Su, Z., Liu, Y., Huang, Y., Zhou, Y., Xie, Q., Yao, S., 2014. Sensitive square wave anodic stripping voltammetric determination of Cd^{2+} and Pb^{2+} ions at Bi/Nafion/overoxidized 2-mercaptoethanesulfonate-tethered polypyrrole/glassy carbon electrode. Sens. Actuat. B Chem. 191, 94–101.

Committee, A.M., 1987. Recommendations for the definition, estimation and use of the detection limit. Analyst 112, 199–204.

De Lima, C.A., Spinelli, A., 2013. Electrochemical behavior of progesterone at an ex situ bismuth film electrode. Electrochim. Acta 107, 542–548.

Dimovasilis, P.A., Prodromidis, M.I., 2013. Bismuth-dispersed xerogel-based composite films for trace Pb(II) and Cd(II) voltammetric determination. Anal. Chim. Acta 769, 49–55.

Dong, Y.P., Huang, L., Zhang, J., Chu, X.F., Zhang, Q.F., 2012. Electro-oxidation of ascorbic acid at bismuth sulfide nanorod modified glassy carbon electrode. Electrochim. Acta 74, 189–193.

El Rhazi, M., Majid, S., 2014. Electrochemical sensors based on polydiaminonaphthalene and polyphenylenediamine for monitoring metal pollutants. Trends Environ. Anal. Chem. 2, 33–42.

Hathoot, A.A., Yousef, U.S., Shatla, A.S., Abdel-Azzem, M., 2012. Voltammetric simultaneous determination of glucose, ascorbic acid and dopamine on glassy carbon electrode modified byNiNPs@poly 1,5-diaminonaphthalene. Electrochim. Acta 85, 531–537.

Henríquez, C., Laglera, L.M., Alpizar, M.J., Calvo, J., Arduini, F., Cerdà, V., 2012. Cadmium determination in natural water samples with an automatic multisyringe flow injection system coupled to a flow-through screen printed electrode. Talanta 96, 140–146.

Hočevar, S.B., Švancara, I., Vytřas, K., Ogorevc, B., 2005. Novel electrode for electrochemical stripping analysis based on carbon paste modified with bismuth powder. Electrochimica Acta 51, 706–710.

Hwang, G.-H., Han, W.-K., Park, J.-S., Kang, S.-G., 2008a. Determination of trace metals by anodic stripping voltammetry using a bismuth-modified carbon nanotube electrode. Talanta 76, 301–308.

Hwang, G.-H., Han, W.-K., Park, J.-S., Kang, S.-G., 2008b. An electrochemical sensor based on the reduction of screen-printed bismuth oxide for the determination of trace lead and cadmium. Sens. Actuat. B Chem. 135, 309–316.

Jain, R., Sharma, R., 2012. Novel bismuth/multi-walled carbon nanotubes-based electrochemical sensor for the determination of neuroprotective drug cilostazol. J. Appl. Electrochem. 42, 341–348.

Jain, R., Tiwari, D.C., Shrivastava, S., 2014. Polyaniline–bismuth oxide nanocomposite sensor for quantification of anti-parkinson drug pramipexole in solubilized system. Mater. Sci. Eng.: B 185, 53–59.

Kefala, G., Economou, A., Voulgaropoulos, A., 2004. A study of Nafion-coated bismuth-film electrodes for the determination of trace metals by anodic stripping voltammetry. Analyst 129, 1082.

Kefala, G., Economou, A., 2006. Polymer-coated bismuth film electrodes for the determination of trace metals by sequential-injection analysis/anodic stripping voltammetry. Anal. Chim. Acta 576, 283–289.

Kokkinos, C., Economou, A., 2011. Disposable Nafion-modified micro-fabricated bismuth-film sensors for voltammetric stripping analysis of trace metals in the presence of surfactants. Talanta 84, 696–701.

Lee, J.-W., Park, D.-S., Shim, Y.-B., Park, S.-M., 1992. Electrochemical characterization of Poly (1, 8-diaminonaphthalene): a functionalized polymer. J. Electrochem. Soc. 139, 3507–3514.

Lezi, N., Vyskocil, V., Economou, A., Barek, J., 2012. Electroanalysis of organic compounds at bismuth electrodes: a short review. Sens. Electroanal. 7, 71–78.

Li, J., Guo, S., Zhai, Y., Wang, E., 2009. High-sensitivity determination of lead and cadmium based on the Nafion–graphene composite film. Anal. Chim. Acta 649, 196–201.

Luo, J.H., Jiao, X.X., Li, N.B., Luo, H.Q., 2013. Sensitive determination of Cd(II) by square wave anodic stripping voltammetry with in situ bismuth-modified multiwalled carbon nanotubes doped carbon paste electrodes. J. Electroanal. Chem. 689, 130–134.

Luo, L., Wang, X., Ding, Y., Li, Q., Jia, J., Deng, D., 2010. Voltammetric determination of Pb^{2+} and Cd^{2+} with montmorillonite-bismuth-carbon electrodes. Appl. Clay Sci. 50, 154–157.

Majid, S., El Rhazi, M.E., Amine, A., Curulli, A., Palleschi, G., 2003. Carbon paste electrode bulk-modified with the conducting polymer Poly(1,8-Diaminonaphthalene): application to lead determination. Microchim. Acta 143, 195–204.

Mariame, C., El Rhazi, M., Adraoui, I., 2009. Determination of traces of copper by anodic stripping voltammetry at a rotating carbon paste disk electrode modified with poly(1,8-diaminonaphtalene). J. Anal. Chem. 64, 632–636.

Miller, J.N., Miller, J.C., 2005. Statistics and Chemometrics for Analytical Chemistry. Pearson/Prentice Hall, Harlow, England, New York.

Nguyen, D.T., Tran, L.D., Le Nguyen, H., Nguyen, B.H., Van Hieu, N., 2011. Modified interdigitated arrays by novel poly(1,8-diaminonaphthalene)/carbon nanotubes composite for selective detection of mercury(II). Talanta 85, 2445–2450.

Ojani, R., Raoof, J.-B., Zavvarmahalleh, S.R.H., 2008. Electrocatalytic oxidation of methanol on carbon paste electrode modified by nickel ions dispersed into poly (1,5-diaminonaphthalene) film. Electrochim. Acta 53, 2402–2407.

Oyama, N., Sato, M., Ohsaka, T., 1989. Preparation of thin polymeric films on electrode surfaces by electro-polymerization of aromatic compounds with amino groups. Synth. Metals 29, 501–506.

Oztekin, Y., Ramanaviciene, A., Ryskevic, N., Yazicigil, Z., Üstündağ, Z., Solak, A.O., Ramanavicius, A., 2011. 1,10-Phenanthroline modified glassy carbon electrode for voltammetric determination of cadmium(II) ions. Sens. Actuat. B: Chem. 157, 146–153.

Philips, M.F., Gopalan, A.I., Lee, K.-P., 2012. Development of a novel cyano group containing electrochemically deposited polymer film for ultrasensitive simultaneous detection of trace level cadmium and lead. J. Hazard. Mater. 237–238, 46–54.

Piankova, L.A., Malakhova, N.A., Stozhko, N.Y., Brainina, K.Z., Murzakaev, A.M., Timoshenkova, O.R., 2011. Bismuth nanoparticles in adsorptive stripping voltammetry of nickel. Electrochem. Commun. 13, 981–984.

Pierini, G.D., Granero, A.M., Di Nezio, M.S., Centurión, M.E., Zon, M.A., Fernández, H., 2013. Development of an electroanalytical method for the determination of lead in Argentina raw propolis based on bismuth electrodes. Microchem. J. 106, 102–106.

Shahrokhian, S., Azimzadeh, M., Amini, M.K., 2015. Modification of glassy carbon electrode with a bilayer of multiwalled carbon nanotube/tiron-doped polypyrrole: application to sensitive voltammetric determination of acyclovir. Mater. Sci. Eng.: C 53, 134–141.

Švancara, I., Prior, C., Hočevar, S.B., Wang, J., 2010. A decade with bismuth-based electrodes in electroanalysis. Electroanalysis 22, 1405–1420.

Švancara, I., Baldrianová, L., Tesařová, E., Hočevar, S.B., Elsuccary, S. A.A., Economou, A., Sotiropoulos, S., Ogorevc, B., Vytřas, K., 2006. Recent advances in anodic stripping voltammetry with bismuth-modified carbon paste electrodes. Electroanalysis 18, 177–185.

Tesarova, E., Baldrianova, L., Hocevar, S.B., Svancara, I., Vytras, K., Ogorevc, B., 2009. Anodic stripping voltammetric measurement of trace heavy metals at antimony film carbon paste electrode. Electrochim. Acta 54, 1506–1510.

Urbanová, V., Vytřas, K., Kuhn, A., 2010. Macroporous antimony film electrodes for stripping analysis of trace heavy metals. Electrochem. Commun. 12, 114–117.

Vu, H.D., Nguyen, L.-H., Nguyen, T.D., Nguyen, H.B., Nguyen, T.L., Tran, D.L., 2015. Anodic stripping voltammetric determination of Cd^{2+} and Pb^{2+} using interpenetrated MWCNT/P1,5-DAN as an enhanced sensing interface. Ionics 21, 571–578.

Wang, J., Lu, J., Hocevar, S.B., Farias, P.A.M., Ogorevc, B., 2000. Bismuth-coated carbon electrodes for anodic stripping voltammetry. Anal. Chem. 72, 3218–3222.

Wang, J., 2005. Stripping analysis at bismuth electrodes: a review. Electroanalysis 17, 1341–1346.

Wang, Z., Li, L., Liu, E., 2013. Graphene ultrathin film electrodes modified with bismuth nanoparticles and polyaniline porous layers for detection of lead and cadmium ions in acetate buffer solutions. Thin Solid Films 544, 362–367.

Xu, H., Zeng, L., Xing, S., Xian, Y., Shi, G., Jin, L., 2008. Ultrasensitive voltammetric detection of trace lead (II) and cadmium (II) using MWCNTs-Nafion/bismuth composite electrodes. Electroanalysis 20, 2655–2662.

Yang, D., Wang, L., Chen, Z., Megharaj, M., Naidu, R., 2014. Voltammetric determination of lead (II) and cadmium (II) using a bismuth film electrode modified with mesoporous silica nanoparticles. Electrochim. Acta 132, 223–229.

Yang, H., Li, J., Lu, X., Xi, G., Yan, Y., 2013. Reliable synthesis of bismuth nanoparticles for heavy metal detection. Mater. Res. Bull. 48, 4718–4722.

Yang, L., Li, Y., 2005. AFM and impedance spectroscopy characterization of the immobilization of antibodies on indium–tin oxide electrode through self-assembled monolayer of epoxysilane and their capture of *Escherichia coli* O157: H7. Biosens. Bioelectron. 20, 1407–1416.

Yi, W.J., Li, Y., Ran, G., Luo, H.Q., Li, N.B., 2012. Determination of cadmium(II) by square wave anodic stripping voltammetry using bismuth–antimony film electrode. Sens. Actuat. B Chem. 166–167, 544–548.

Zhu, L., Xu, L., Huang, B., Jia, N., Tan, L., Yao, S., 2014. Simultaneous determination of Cd(II) and Pb(II) using square wave anodic stripping voltammetry at a gold nanoparticle–graphene–cysteine composite modified bismuth film electrode. Electrochim. Acta 115, 471–477.

Please cite this article in press as: Salih, F.E. et al., Electrochemical detection of lead (II) at bismuth/Poly(1,8-diaminonaphthalene) modified carbon paste electrode. Arabian Journal of Chemistry (2015), http://dx.doi.org/10.1016/j.arabjc.2015.08.021